

# Pressure on charged domain walls and additional imprint mechanism in ferroelectrics

P. Mokrý,<sup>1,\*</sup> A. K. Tagantsev,<sup>2</sup> and J. Fousek<sup>1</sup>

<sup>1</sup>*Department of Electrical Engineering,*

*Technical University of Liberec, CZ-46117 Liberec, Czech Republic*

<sup>2</sup>*Ceramics Laboratory, Materials Department,*

*EPFL Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland*

(Dated: February 6, 2008)

## Abstract

The impact of free charges on the local pressure on a charged ferroelectric domain wall produced by an electric field has been analyzed. A general formula for the local pressure on a charged domain wall is derived considering full or partial compensation of bound polarization charges by free charges. It is shown that the compensation can lead to a very strong reduction of the pressure imposed on the wall from the electric field. In some cases this pressure can be governed by small nonlinear effects. It is concluded that the free charge compensation of bound polarization charges can lead to substantial reduction of the domain wall mobility even in the case when the mobility of free charge carriers is high. This mobility reduction gives rise to an additional imprint mechanism which may play essential role in switching properties of ferroelectric materials. The effect of the pressure reduction on the compensated charged domain walls is illustrated for the case of  $180^\circ$  ferroelectric domain walls and of  $90^\circ$  ferroelectric domain walls with the head-to-head configuration of the spontaneous polarization vectors.

PACS numbers: 77.80.Dj

Keywords: Ferroelectric domain wall, domain structure

## I. INTRODUCTION

Understanding the dynamics of domain wall motion is essential for the explanation of many phenomena in ferroelectric materials. In many models for the evolution of domains in ferroelectrics, researchers deal with systems where charged ferroelectric domain walls appear. Classical examples to be mentioned are the work by Landauer<sup>1</sup> on the nucleation of  $180^\circ$  domains and that by Miller and Weinreich<sup>2</sup> on the sidewise movement of  $180^\circ$  domain walls. In these models, the domain wall dynamics is analyzed by minimizing the thermodynamic potential consisting of the depolarizing field energy, the energy associated with the crystal lattice polarization, the energy of the domain wall, and the energy supplied to the system by the external electric source. It is evident that in all systems where charged domain walls appear there exists a possibility of compensation of bound charges by free charges, which affects the aforementioned energies through the reduction of the net charge at the domain wall. It was already pointed out by Landauer<sup>1</sup> that the process of bound charges compensation will not only reduce the depolarization energy, but it will also reduce the energy supplied to the system by external electric sources. Since the latter energy actually represents the driving force for domain wall motion, one can expect that the appearance of free charges in the system will result in a reduction of local pressure on the domain wall. This may have a serious impact on the domain nucleation and the sidewise domain wall motion. The problem of the impact of bound charge compensation on the domain pattern evolution seems to be of special practical interest for ferroelectric ceramics where the appearance of charged domain walls is readily expected whereas the high temperatures used to pole it can promote free-charge screening effects.

The aforementioned issues have motivated the theoretical analysis presented below, where we will address the effect of bound charge compensation on the local pressure exerted on the walls by the electric field. We will cover the general situation as well as some cases of special interest. In Sec. II we will illustrate the effect of charge compensation for the simplest situation. Section III presents a derivation of the general expression for the local pressure imposed by the electric field to an arbitrarily compensated ferroelectric wall. In Sec. IV we will demonstrate the application of the general results to systems with low electric fields (Subsec. IV A) and to systems where nonlinearity of the dielectric response of the crystal lattice is essential (Subsec. IV B).

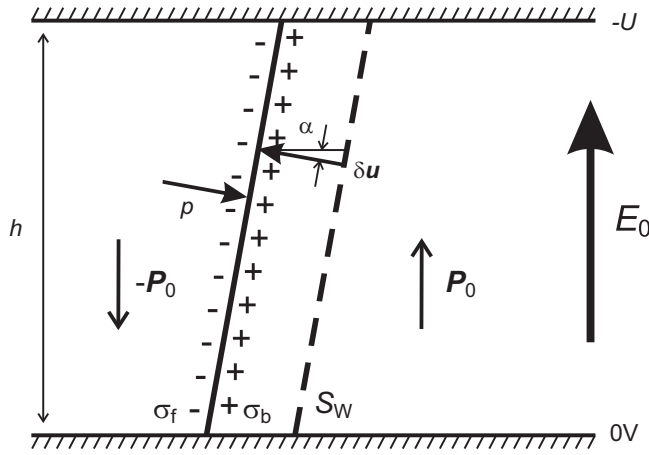


FIG. 1: Scheme of a ferroelectric capacitor of thickness  $h$  with a  $180^\circ$  ferroelectric domain wall tilted by an angle  $\alpha$  with respect to its electro-neutral orientation. Bottom electrode is grounded and top electrode is at a constant electric voltage  $-U$ . Pluses indicate the positive bound charges  $\sigma_b$  due to a discontinuity of the spontaneous polarization  $P_0$  at the domain wall, minuses indicate the free charges  $\sigma_f$  that fully compensate the bound charges. Symbol  $\delta u$  stands for the virtual displacement of the domain wall and symbol  $p$  stands for the external mechanical pressure that should be applied to the wall to keep it at rest.

## II. SIMPLE MODEL WITH FULL CHARGE COMPENSATION

At first we analyze the effect of free charges on the local pressure on a ferroelectric domain wall for the system shown in Fig. 1. We consider the hard ferroelectric approximation where the electric displacement in it is presented as the sum of the constant spontaneous polarization  $\pm P_0$  with antiparallel orientation in neighboring domains and the linear dielectric response of the crystal lattice to the electric field, characterized by the permittivity  $\epsilon$ .

We consider a planar  $180^\circ$  domain wall, which makes angle  $\alpha$  with the vector of spontaneous polarization. We address the situation where the tilt of the domain wall in the clockwise direction yields the appearance of positive bound charges of surface density  $\sigma_b = 2P_0 \sin \alpha$  as it is shown in Fig. 1. The bound charges are completely compensated by free charges of surface density  $\sigma_f = -\sigma_b$ . The bottom electrode is grounded and the top electrode is connected to a source of constant voltage  $-U$ . The voltage applied to the electrodes produces an electric field  $E_0 = U/h$ .

In this study, we calculate the value of local pressure on the ferroelectric domain wall

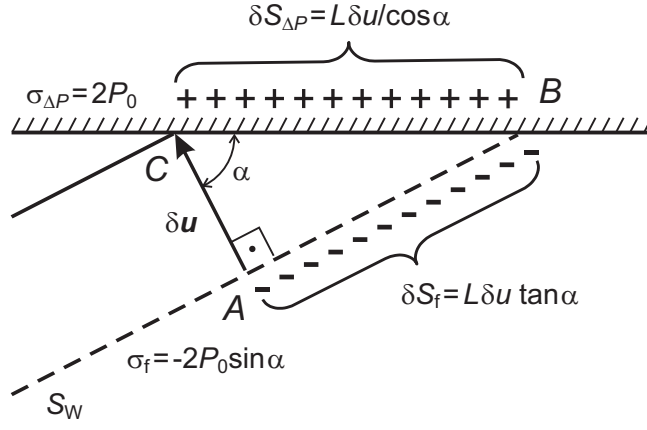


FIG. 2: Detail of the intersection area of the domain wall and the top electrode indicating the charge variation on the top electrode during the virtual displacement of the domain wall. Dashed and solid lines show the original and displaced positions of the domain wall  $S_W$ , respectively. Symbol  $\sigma_{\Delta P}$  stands for the surface charge density of bound charges due to spontaneous polarization reversal during the domain wall shift. Symbol  $\sigma_f$  stands for the surface charge density of free charges at the domain wall. Symbol  $\delta S_{\Delta P}$  indicates the area where spontaneous polarization reversal occurs during the domain wall shift. Symbol  $\delta S_f$  indicates the area of domain wall, which reaches the electrode during the domain wall shift.

produced by the electric field using the principle of virtual displacements. We consider the wall at rest, when the force imposed on it by the electric field is balanced by the external mechanical pressure  $p$ . According to the principle of virtual displacements, the variation of the proper thermodynamic function  $\delta G$  equals the work produced by the external mechanical pressure  $p$  during the virtual displacement, i.e.,  $\delta W_p = -S_W p \delta u$ , where  $S_W$  is the area of the domain wall and  $\delta u$  is the virtual displacement of the domain wall in the normal direction. One readily checks that for the considered model in the hard ferroelectric approximation, the thermodynamic function of the system consists of the electrostatic energy and the energy supplied to the system by external electric sources; it reads:

$$G = \int_V \frac{1}{2} \varepsilon E^2 dV + UQ, \quad (1)$$

where  $\varepsilon$  is the permittivity of the ferroelectric and  $Q$  is the charge on the top electrode. Figure 2 shows in detail the intersection area of the domain wall and the top electrode. The considered virtual displacement is indicated by the line  $AC$ , where  $A$  indicates a point on the domain wall in the original position and  $C$  indicates the same point on the displaced

domain wall. Since the bound charges on the oblique domain wall are considered to be fully compensated by free charges, the electric field in the ferroelectric capacitor is homogeneous and equal to  $E_0 = U/h$ . This means that the variation of the thermodynamic function,  $\delta G$ , which is produced by the virtual displacement  $\delta u$  of domain wall, is given only by the variation of charge on the top electrode,  $\delta Q$ . Thus, we can write the following equation of equilibrium:

$$U \delta Q = -S_W p \delta u. \quad (2)$$

Considering the ferroelectric capacitor of length  $L$  in the direction perpendicular to the cross-section shown in Fig. 1, the area of oblique domain wall equals

$$S_W = Lh / \cos \alpha. \quad (3)$$

The variation of charge on the top electrode  $\delta Q$  includes the charge  $\delta Q_{\Delta P}$  due to the spontaneous polarization reversal, which is partially compensated by the free charge  $\delta Q_f$  that has arrived at the top electrode from the “annihilated” part of the wall during its virtual displacement  $\delta u$  in the normal direction. Thus it is  $\delta Q = \delta Q_{\Delta P} + \delta Q_f$ . The charge  $\delta Q_{\Delta P}$  is provided by the bound charge density  $\sigma_{\Delta P} = 2P_0$  due to spontaneous polarization reversal, which occurs on the area  $\delta S_{\Delta P}$  on the top electrode indicated by the line  $BC$  in Fig. 2. Using trigonometric functions one can readily get the relation between the virtual displacement of the domain wall  $\delta u$  and the area  $\delta S_{\Delta P} = L\delta u / \cos \alpha$ . Thus the spontaneous polarization reversal produces the variation of charge on the top electrode  $\delta Q_{\Delta P} = -\sigma_{\Delta P} \delta S_{\Delta P} = -2P_0 L \delta u / \cos \alpha$ . The charge  $\delta Q_f$  equals the free charge from the piece of the domain wall that “annihilates” at the electrode during the virtual displacement of the domain wall. This charge has a surface density of  $\sigma_f = -2P_0 \sin \alpha$  and is distributed on the area  $\delta S_f$  on the domain wall indicated by the line  $AB$  in Fig. 2. Using trigonometric functions, it is easy to express the relation between the virtual domain wall displacement  $\delta u$  and the area  $\delta S_f = -\sigma_f \delta S_f = 2LP_0 \delta u (\sin \alpha) / (\tan \alpha)$ . Finally, one can present the variation of the charge on the top electrode in the form:

$$\delta Q = -2P_0 L (1 - \sin^2 \alpha) \delta u / \cos \alpha. \quad (4)$$

Substituting Eqs. (3) and (4) into (2) we get the formula for the local mechanical pressure on an inclined  $180^\circ$  domain wall, which is fully compensated with free charges:

$$p = 2P_0 E_0 (1 - \sin^2 \alpha). \quad (5)$$

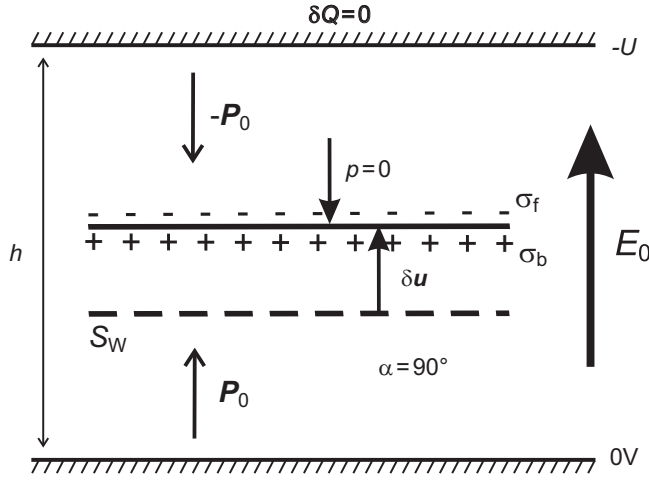


FIG. 3: Special case of a fully compensated domain wall, which is parallel to the electrodes (i.e.  $\alpha = 90^\circ$ ). In this case, shift  $\delta u$  of the domain wall  $S_W$  in the normal direction does not produce any change of charge on the top electrode,  $\delta Q = 0$ , resulting in zero local pressure on such a domain wall.

It is seen that, for the domain wall that is normal to the electrode, i.e.  $\alpha = 0$ , the above formula reduces to the well-known value of pressure  $2P_0E$  on an uncharged  $180^\circ$  domain wall. Figure 3 shows the opposite extreme case of a fully compensated domain wall, which is parallel to the electrodes (i.e.  $\alpha = 90^\circ$ ). This case corresponds to a fully compensated head-to-head configuration of the spontaneous polarization. In this situation, according to Eq. (5) the local mechanical pressure on the domain wall is zero. This can be readily understood. Indeed, in this case, the shift of domain wall  $\delta u$  does not produce any change in the thermodynamic function  $G$ , since a displacement of the fully compensated wall should affect neither the electric field nor the charge on the top electrode.

### III. LOCAL PRESSURE ON A FERROELECTRIC DOMAIN WALL

In this section we obtain a formula for the local pressure on the ferroelectric domain wall for the most general situation where (i) the electric field is inhomogeneous, (ii) wall configuration is arbitrary, (iii) charge compensation of the wall is not assumed to be full, and (iv) the analysis goes beyond the hard ferroelectric approximation. The only limitation of the presented analysis would be the neglect of the mechanical effects, i.e. we set the mechanical stress  $\tau_{ij}^{\text{mech}}$  zero everywhere in the sample. Whenever such effects are essential

they may be incorporated in the framework.

The desired formula can be obtained by application of the virtual displacement method to a general configuration of electrodes and arbitrary compensated ferroelectric domain walls (see Appendix A). However, the calculations can be essentially simplified by using an advanced thermodynamic result derived in the classical textbook by Landau and Lifshitz<sup>6</sup>. According to this book, the volume force density  $f_i$  in a dielectric can be presented in the form

$$f_i = \frac{\partial \tau_{ij}}{\partial x_j} \quad (6)$$

in term of the generalized stress tensor  $\tau_{ij}$  which, in turn, can be written as

$$\tau_{ij} = \tilde{\Phi} \delta_{ij} + \tau_{ij}^{\text{mech}} + \frac{1}{2} (E_i D_j + E_j D_i) \quad (7)$$

with

$$\tilde{\Phi} = \Phi - (1/2) \varepsilon_0 E^2 - E_i P_i \quad (8)$$

where  $P_i$  and  $D_i = P_i + \varepsilon_0 E_i$  are the polarization and electrical displacement, respectively;  $\Phi$  is the thermodynamic function of the dielectric characterized by the differential  $d\Phi = E_i dP_i + \tau_{ij}^{\text{mech}} du_{ij}$  where  $u_{ij}$  is the strain tensor.

Applying Eq. (6) to the two domains in the vicinity of a domain wall, one presents the pressure to the latter  $p$  in the form

$$p = [[\tau_{ij}]] n_i n_j \quad (9)$$

where  $n_i$  is vector normal to the wall. The notation  $[[Z]]$  here and therein is used to denote the jump of the variable  $Z$  at the wall. Considering the mechanically free ferroelectric sample, i.e.  $\tau_{ij}^{\text{mech}} = 0$ , and combining Eqs. (7) and (9) one gets

$$p = [[\tilde{\Phi}]] + [[E_i D_j]] n_i n_j. \quad (10)$$

If we further employ the expressions for the continuity of tangential components of the electric field at the domain wall  $[[E_{t,i}]] = [[E_i - (E_k n_k) n_i]] = 0$ , the relation for the normal component of electric displacement at the domain wall  $[[D_i]] n_i = \sigma_f$ , and the algebraic identity

$$[[E_i D_j]] = \hat{E}_i [[D_j]] + [[E_i]] \hat{D}_j, \quad (11)$$

where  $\widehat{E}_i = (E_i^{(1)} + E_i^{(2)})/2$  is the average electric field at the opposite sides of the domain wall, we get the formula for the external mechanical pressure on the domain wall

$$p = [[\widetilde{\Phi} + (1/2) \varepsilon_0 E^2 + P_i E_i]] - \widehat{E}_i ([[P_i]] - \sigma_f n_i). \quad (12)$$

Considering Eq. (8), formula (12) can be further simplified:

$$p = \Phi^{(2)} - \Phi^{(1)} - \frac{1}{2} \left( E_i^{(1)} + E_i^{(2)} \right) \left( P_i^{(2)} - P_i^{(1)} - \sigma_f n_i \right). \quad (13)$$

Here upper indexes (1) and (2) specify to which domain the variable is referred to, the direction of the normal vector  $n_i$  is taken inside domain (2), and the pressure is considered as positive when acting from domain (2) to domain (1).

#### IV. PRESSURE ON THE WALL IN SPECIAL CASES

In this section, we present consequences of Eq. (13) and demonstrate its applicability for two particular cases. At first we present further a simplification of formula (13) for the case of low applied fields where the dielectric non-linearity of the ferroelectric can be neglected. Then we demonstrate the application of formula (13) in systems where the non-linearity of the dielectric response of the crystal lattice is essential.

##### A. Hard ferroelectric approximation

For small electric fields we can use the “hard ferroelectric” approximation and express the polarization as a sum of the constant spontaneous polarization  $P_{0,i}$  and the linear response of the polarization of the crystal lattice to the electric field

$$P_i \approx P_{0,i} + \chi_{ij} E_j, \quad (14a)$$

where  $\chi_{ij}$  is the susceptibility of the ferroelectric. In this situation, function  $\Phi(P)$  can be expressed in a form

$$\Phi(P) \approx \frac{1}{2} \chi_{ij} E_i E_j. \quad (14b)$$

After substitution of Eqs. (14) into Eq. (13) one readily gets

$$p = -\widehat{E}_i ([[P_{0,i}]] - \sigma_f n_i) - \frac{1}{2} [[\chi_{ij}]] E_i^{(1)} E_j^{(2)}. \quad (15)$$



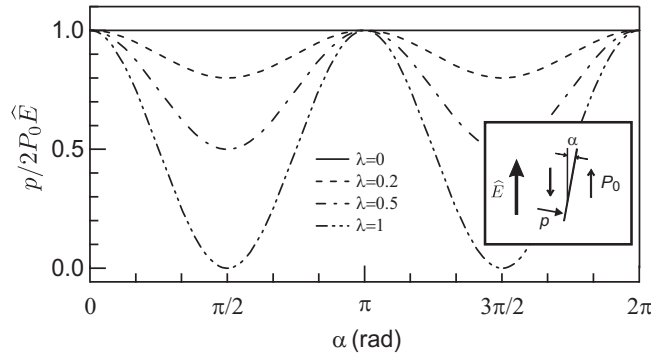


FIG. 4: Normalized pressure on  $180^\circ$  ferroelectric domain wall versus the tilt of domain wall  $\alpha$  with respect to vectors of spontaneous polarization, which is shown in the inset, for different degrees of compensation of bound charge  $\sigma_b$  by free charge  $\sigma_f$ ;  $\lambda = -\sigma_f/\sigma_b$ .

In the case of absence of free charges in the system, Eq. (15) was obtained earlier<sup>3,4</sup>.

Two numerical examples of the effect of free charges on the local pressure on a charged ferroelectric domain wall are shown in Figs. 4 and 5. In Fig. 4 we consider the case of a  $180^\circ$  ferroelectric domain wall where the vector of average electric field  $\hat{E}_i$  is considered to be always parallel to the vectors of spontaneous polarization  $P_{0,i}$  and the domain wall is considered to be tilted by an angle  $\alpha$  with respect to the directions of spontaneous polarization. The tilt of the domain wall results in the appearance of bound charge on the domain wall,  $\sigma_b$ , and the local pressure of external sources on such a wall equals  $2P_{0,i}\hat{E}_i$  and its direction is shown in the inset of Fig.4. Then we consider that the bound charge is partially compensated by free charges  $\sigma_f$ . The degree of partial compensation is expressed by the quantity  $\lambda$ , so that  $\sigma_f = -\lambda\sigma_b$  where  $0 \leq \lambda \leq 1$ . It is seen that free charges reduces the value of pressure  $p$ , but the important point is that, for the same degree of screening  $\lambda$ , the value of  $p$  varies depending on the domain wall tilt. Zero pressure corresponds to the situation of full compensation of the domain wall, which is perpendicular to the vectors of spontaneous polarization.

The effect of free charge compensation on the pressure on a charged  $90^\circ$  domain wall is shown in Fig. 5. However, the contribution due to dielectric anisotropy is neglected (i.e.  $[[\chi_{ij}]] = 0$ ), since it produces a field redistribution<sup>5</sup>, which can be hardly evaluated in the general case. Since this type of domain wall is ferroelastic it is reasonable to consider that the angle between the vectors of spontaneous polarization and the domain wall is fixed as it is indicated in the inset of Fig. 5. The domain wall charge is equal to  $\sigma_b = \sqrt{2}P_0$  and

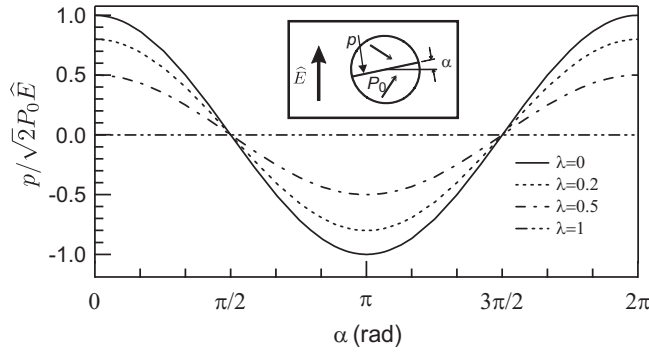


FIG. 5: Normalized pressure on a  $90^\circ$  ferroelectric domain wall versus the angle,  $\alpha$ , between the normal to the wall and the vector of electric field, which is shown in the inset, for different degrees of compensation of bound charge  $\sigma_b$  by free charges  $\sigma_f$ ;  $\lambda = -\sigma_f/\sigma_b$ . Note that for complete screening of bound charges, i.e.  $\lambda = 1$ , the local pressure on the domain wall is zero for any relative orientation of the domain wall and the electric field. Here the contribution due to the dielectric anisotropy is neglected, i.e.  $[[\chi_{ij}]] = 0$

the local pressure is a function of the tilt of the domain wall with respect to the average electric field  $\hat{E}_i$ . It is seen that, in this case, the presence of free charges leads to an effective decrease of the value of spontaneous polarization. The physical reason for this is that in this case the vector  $[[P_{0,i}]]$  is always parallel to the normal vector of the domain wall  $n_i$ . It is noticeable that, in the case of the complete bound charge compensation, the pressure on the domain wall is zero regardless the orientation of the average electric field and the domain wall.

## B. Nonlinear effects

Formula (13) makes it possible to analyze the effects of the dielectric nonlinearity of the crystal lattice on the local pressure  $p$ . As an example we consider a fully compensated  $180^\circ$  domain wall, which is perpendicular to the vectors of spontaneous polarization (see Fig. 2). In section II we have shown that, in the hard ferroelectric approximation, the local pressure on such a wall is zero. However, analysis beyond this approximation shows that this force is not actually zero. Let us find this force for the case of a uniaxial ferroelectric with the

second order phase transition. In this case, the free energy of the ferroelectric reads:

$$\Phi(P) = \Phi_0 + \frac{1}{2}\alpha P^2 + \frac{1}{4}\beta P^4, \quad (16)$$

where, in the ferroelectric phase,  $\alpha < 0$  and  $\beta > 0$ . Discontinuous change of polarization states  $P^{(1)}$  and  $P^{(2)}$  at the domain wall and the presence of free charges  $\sigma_f$  produce the electric field  $\Delta E$  according to the equation:

$$P^{(2)} - P^{(1)} - \sigma_f = 2\varepsilon_0 \Delta E. \quad (17a)$$

This electric field is of antiparallel orientation at the opposite sides of the domain wall and it is superposed on the uniform applied electric field  $E_0$ , so that the equation of state in the adjacent domains are of a form:

$$\partial\Phi(P^{(1)})/\partial P = E_0 + \Delta E, \quad (17b)$$

$$\partial\Phi(P^{(2)})/\partial P = E_0 - \Delta E. \quad (17c)$$

The polarization  $P^{(1)}$  and  $P^{(2)}$  at the opposite sides of the domain wall is given by the solution of Eqs. (17) and, in the case of fully compensated domain wall, i.e.,  $\sigma_f = -2P_0$ , it can be expanded in a Taylor series with respect to the applied electric field  $E_0$ :

$$P^{(1)} \approx P_0 + \chi E_0 - \frac{3\varepsilon_0\chi^2}{2P_0(\chi + \varepsilon_0)} E_0^2 + \dots, \quad (18a)$$

$$P^{(2)} \approx -P_0 + \chi E_0 + \frac{3\varepsilon_0\chi^2}{2P_0(\chi + \varepsilon_0)} E_0^2 + \dots, \quad (18b)$$

where  $P_0 = \sqrt{-\beta/\alpha}$  is the spontaneous polarization and  $\chi = -1/(2\alpha)$  is the dielectric susceptibility of the crystal lattice. After substitution of Eqs. (18) into Eq. (16), we can readily obtain the expansion of function  $\Phi(P)$  at the opposite sides of the domain wall in terms of the applied electric field:

$$\Phi(P^{(1)}) \approx -\frac{P_0^2}{8\chi} + \frac{1}{2}\chi E_0^2 + \frac{\chi^2(\chi - 2\varepsilon_0)}{2P_0(\chi + \varepsilon_0)} E_0^3 + \dots, \quad (19a)$$

$$\Phi(P^{(2)}) \approx -\frac{P_0^2}{8\chi} + \frac{1}{2}\chi E_0^2 - \frac{\chi^2(\chi - 2\varepsilon_0)}{2P_0(\chi + \varepsilon_0)} E_0^3 + \dots. \quad (19b)$$

When one considers that the average field in the ferroelectric,  $\hat{E}$ , is dominated by the applied electric field  $E_0$ , i.e.  $\hat{E} = E_0$ , the resulting formula for the pressure on the domain wall is according to Eq. (13) equal to:

$$p \approx -(\chi^2/P_0) E_0^3, \quad (20)$$

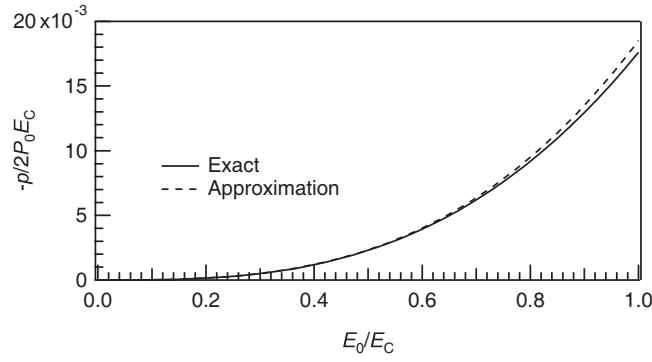


FIG. 6: The applied field dependence of the local pressure on a fully compensated head-to-head  $180^\circ$  ferroelectric domain wall. The pressure is normalized to  $-2P_0E_C$ , that equals the value of pressure expected to be applied to an uncompensated domain wall at the thermodynamic coercive field  $E_C$  in the hard ferroelectric approximation. The field is normalized to the thermodynamic coercive field  $E_C$ . The exact values (solid line) obtained by numerical solving the nonlinear Eqs. (17) are compared with the approximative values (dashed line) calculated using the formula (20).

which means that the pressure on the domain wall is oriented in the opposite direction than the “expected”  $2P_0E_0$  contribution.

The physical interpretation of the above formula is as follows. The application of a high electric field to the ferroelectric sample with the considered configuration of a fully compensated charged  $180^\circ$  domain wall is associated with two effects: first, it produces the difference in volume energy density of the crystal lattice at the opposite sides of the domain wall due to dielectric nonlinearity of the crystal lattice, and second, it produces an additional charging of the domain wall due to a different polarization response at opposite sides of the domain wall so that the wall becomes negatively charged. The pressure associated with the electrostatic force acting on this charge is directed against that associated with the energy difference. Finally, the resulting formula corresponds to the sum of these effects.

Figure 6 shows the applied electric field dependence of the local pressure on a fully compensated domain wall, which is parallel to the electrodes (see Fig. 3). The dashed line shows the approximative result given by formula (20). The solid line shows the exact result given by the numeric solution of the system of nonlinear equations (17), where the function  $\Phi(P)$  is given by Eq. (16). In Fig. 6, numerical values typical for barium titanate were used:  $P_0 = 0.26 \text{ Cm}^{-2}$  and  $\chi = 188 \varepsilon_0$ . It is seen that Eq. (20) provides a very good approximation, which differs only by about 6% from the exact value at the thermodynamic

coercive field  $E_C = P_0 / (3\sqrt{3}\chi)$ .

## V. ADDITIONAL IMPRINT MECHANISM

The results obtained in the previous sections enable us to draw a conclusion on the imprint behavior of polydomain ferroelectrics.

Imprint is a property of a ferroelectric capacitor of exhibiting a higher switching voltage when the switching starts from a state in which the capacitor has been kept for a long time or subjected to light illumination (see Ref.<sup>7</sup> for comprehensive discussion). A popular and widely referred to imprint mechanism, which has been offered by the Sandia Laboratory group<sup>8,9</sup>, is related to free-carrier compensation of charged domain walls. Our analysis presented in this paper suggests that this compensation should lead to one more imprint mechanism.

The key issue of the Sandia mechanism, which we will refer to as “trapping imprint”, is that, if the free carriers compensating the bound charge of a wall are trapped, then the mobility of this wall is deteriorated since now it is to drag with it the weakly mobile trapped carriers. Since, in typically low-conductive ferroelectrics, an appreciable time or/and illumination is needed for the free-carrier compensation of the bound charge of a wall, this effect will lead to the imprint. In the context of the analysis presented above it is clear that the aforementioned charge compensation will also lead to a reduction of the “thermodynamic” (pondermotive) force applied to the wall in the switching field. This reduction, similarly to the above case, can manifest itself in an imprint mechanism, which we will refer to as “force-reduction” imprint. One should stress that the performance of these mechanisms can be appreciably different. For instance, in the case of trapping imprint, if the switching field is applied long enough to let the trapped charges drift with the wall, the imprint effect becomes weaker. Its efficiency is clearly controlled by the mobility of the trapped free carriers; in the limit of high mobility the effect vanishes. On the other hand, the force-reduction imprint is clearly insensitive to the mobility of the compensating free chargers. In contrast to the trapping imprint, one cannot cope with this mechanism by using longer switching pulses. All in all, one sees a possibility to distinguish these imprint mechanisms in real ferroelectric systems.

## VI. CONCLUSIONS

The impact of free charges on the local pressure on a charged ferroelectric domain wall produced by an electric field has been analyzed. A general formula for the local pressure on a charged domain wall is derived considering full or partial compensation of the bound polarization charge with the free charge. It is shown that the compensation can lead to a very strong reduction of the pressure imposed on the wall by the electric field. In some cases this pressure can be governed by small nonlinear effects. It is concluded that the free charge compensation of the bound polarization charge can lead to substantial reduction of the domain wall mobility even in the case of the high mobility of the free charge. This mobility reduction gives to an additional imprint mechanism which may play essential role in switching properties of ferroelectric materials. Using this mechanism, it is possible to explain frequent observations of very stable domain patterns with the head-to-head configuration of the vectors of spontaneous polarization<sup>10</sup>. The results obtained can be used in modeling the poling of ferroelectric ceramics, domain nucleation, sidewise domain wall movement and spontaneous polarization switching in imprinted, leaky ferroelectric samples, and samples treated at elevated temperatures.

### Acknowledgments

This project was supported by the Swiss National Science Foundation and by the Grant Agency of the Czech Republic, project GACR 202/06/0411. Authors acknowledge Guido Gerra for reading the manuscript.

---

\* Electronic address: pavel.mokry@tul.cz

<sup>1</sup> R. Landauer, J. Appl. Phys. **28**, 227 (1957).

<sup>2</sup> R. C. Miller and G. Weinreich, Phys. Rev. **117**(6), 1460 (1960).

<sup>3</sup> V. N. Nechaev and A. M. Roschupkin, Sov. Phys. Solid State **30**(8), 1319 (1988)

<sup>4</sup> H. Kessler, H. Balke, J. Mech. Phys. Sol. **54**, 113 (2006)

<sup>5</sup> J. Novak, J. Fousek, J. Maryska and M. Marvan, Ferroelectrics **319**, 417-424 (2005)

- <sup>6</sup> L. D. Landau, E. M. Lifshitz, *Electrodynamics of Continuous Media*, Oxford: Pergamon Press, 1984
- <sup>7</sup> A. K. Tagantsev and G. Gerra, J. Appl.Phys. **100**, 051607 (2006)
- <sup>8</sup> W. L. Warren, D. Dimos, G. E. Pike, B. A. Tuttle, M. V. Raymond, R. Ramesh, and J. T. Evans, Applied Physics Letters, **67**, 866-868 (1995)
- <sup>9</sup> W. L. Warren, D. Dimos, B. A. Tuttle, G. E. Pike, R. W. Schwartz, P. J. Clew, and D. C. McIntyre, J. Appl. Phys., **77**, 6695-702 (1995)
- <sup>10</sup> B. J. Rodriguez, A. Gruverman, A. I. Kingon, R. J. Nemanich, and J. S. Cross, J. Appl. Phys. 95(4), 1958 (2004)

## APPENDIX A: LOCAL PRESSURE ON A FERROELECTRIC DOMAIN WALL DERIVED FROM THE PRINCIPLE OF VIRTUAL DISPLACEMENTS

In this Appendix we offer an alternative derivation of the local pressure on ferroelectric domain wall than it is presented in Sec. III. Here, we use again the principle of virtual displacements as we do in Sec. II. We consider a system shown in Fig. 7 where inside a ferroelectric material with polarization  $P_i^{(1)}$  there exists a domain of the material with a different polarization state  $P_i^{(2)}$ , i.e. that there is a discontinuity of the polarization across the interface  $S_W$ . This interface splits the ferroelectric into two domains, which have volumes  $V^{(1)}$  and  $V^{(2)}$ , respectively. Inside each domain there is a conductor, which carries charge  $Q_E^{(1)}$  and  $Q_E^{(2)}$ , respectively, and has electric potential  $\varphi_E^{(1)}$  and  $\varphi_E^{(2)}$ , respectively. We consider that bound charges due to discontinuous change of polarization at the domain wall  $S_W$  are partially compensated by free charges of surface density  $\sigma_f$ . The charges on conductors and on the domain wall produce electric fields  $E_i^{(1)}$  and  $E_i^{(2)}$  within each domain. Symbols  $\varphi^{(1)}$  and  $\varphi^{(2)}$  stand for electric potentials within each domain.

In order to obtain a general formula for the external mechanical pressure  $p$  on the domain wall, we follow the principle of virtual displacements presented in Section II. However, we adopt the thermodynamic function  $G$  in a more general form:

$$G = \int_V \left[ \Phi(P) + \frac{1}{2} \varepsilon_0 E^2 \right] dV - \sum_i \varphi_E^{(i)} Q_E^{(i)}, \quad (\text{A1})$$

The first term in the above formula represents the energy associated with the polarization of crystal lattice of ferroelectric,  $\Phi(P)$ , and the electric field energy,  $(1/2)\varepsilon_0 E^2$ , which are

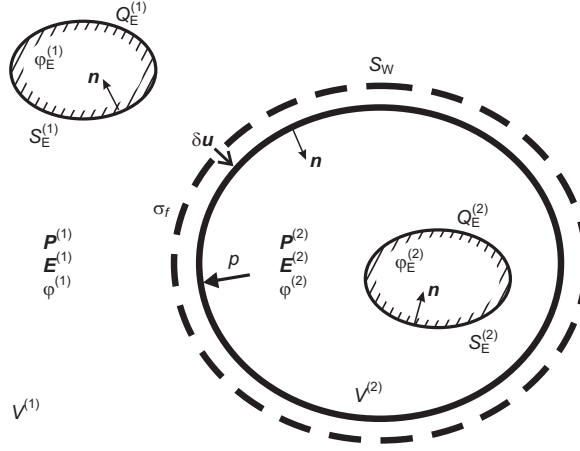


FIG. 7: Configuration used to calculate the local pressure imposed by the electric field to a wall. Domain wall  $S_W$  separates the ferroelectric into two domains of volumes  $V^{(1)}$  and  $V^{(2)}$ . There are two conductors, which carry charges  $Q_E^{(1)}$  and  $Q_E^{(2)}$  and have electric potentials  $\varphi_E^{(1)}$  and  $\varphi_E^{(2)}$  within each domain. The bulk quantities within each domain are the polarization  $P_i^{(1)}$  and  $P_i^{(2)}$ , electric field  $E_i^{(1)}$  and  $E_i^{(2)}$  and electric potential  $\varphi^{(1)}$  and  $\varphi^{(2)}$ . Symbol  $\delta u$  stands for the virtual displacement of the domain wall and symbol  $p$  stands for the external mechanical pressure that should be applied to the wall to keep it at rest.

integrated over the volume  $V$  of ferroelectric. The second term in Eq. (A1) represents the subtracted work of the electric sources. It should be also noticed that the thermodynamic function  $G$  given by Eq. (A1) is used just for convenience; the result (equation of state) is independent of the choice of the potential as always.

In what follows it is convenient to transform the work of electric sources into volume integrals:

$$\varphi_E^{(1)} Q_E^{(1)} = -\varphi_E^{(1)} \int_{S_E^{(1)}} D_i^{(1)} n_i dS = \int_{V^{(1)}} E_i^{(1)} D_i^{(1)} dV + \int_{S_W} \varphi^{(1)} D_i^{(1)} n_i dS, \quad (\text{A2a})$$

$$\varphi_E^{(2)} Q_E^{(2)} = -\varphi_E^{(2)} \int_{S_E^{(2)}} D_i^{(2)} n_i dS = \int_{V^{(2)}} E_i^{(2)} D_i^{(2)} dV - \int_{S_W} \varphi^{(2)} D_i^{(2)} n_i dS, \quad (\text{A2b})$$

where  $D_i^{(1)}$  and  $D_i^{(2)}$  are the vectors of electric displacement in domains  $V^{(1)}$  and  $V^{(2)}$ , respectively. In the derivation of the above equations, we consider the absence of free charges, i.e.  $\text{div } D_i = 0$ , inside domains  $V^{(1)}$  and  $V^{(2)}$  and vanishing the surface integral over the domain  $V^{(1)}$  at infinity. Orientation of the normal vectors  $n_i$  is indicated in Fig. 7. If we further employ the expressions for electric displacement  $D_i = P_i + \varepsilon_0 E_i$ , the continuity



of the electric potential at the domain wall  $[[\varphi]] = 0$ , the continuity of the normal component of electric displacement at the domain wall  $[[D_i]] n_i = \sigma_f$ , and the algebraic identity used in Eq. (11), the thermodynamic function  $G$  can be expressed in the form:

$$\begin{aligned} G = & \int_{V^{(1)}} \left[ \Phi^{(1)}(P^{(1)}) - \frac{1}{2} \varepsilon_0 E_i^{(1)} E_i^{(1)} - E_i^{(1)} P_i^{(1)} \right] dV + \\ & + \int_{V^{(2)}} \left[ \Phi^{(2)}(P^{(2)}) - \frac{1}{2} \varepsilon_0 E_i^{(2)} E_i^{(2)} - E_i^{(2)} P_i^{(2)} \right] dV + \\ & + \int_{S_W} \hat{\varphi} \sigma_f dS. \end{aligned} \quad (\text{A3})$$

For the sake of presentation, it will be useful to define functions

$$\tilde{\Phi}_B = \Phi(P) - \frac{1}{2} \varepsilon_0 E_i E_i - E_i P_i, \quad (\text{A4a})$$

$$\tilde{\Phi}_S = \hat{\varphi} \sigma_f \quad (\text{A4b})$$

and to write the function  $G$  in the form

$$G = \int_V \tilde{\Phi}_B dV + \int_{S_W} \tilde{\Phi}_S dS, \quad (\text{A5})$$

where the volume integral is taken over the volume  $V = V^{(1)} + V^{(2)}$ .

Now our task is to express the variation of thermodynamic function  $\delta G$ , which is produced by the virtual displacement of domain wall:

$$\delta G = \int_V \delta \tilde{\Phi}_B dV + \int_{S_W} \delta \tilde{\Phi}_S dS - \int_{S_W} \left\{ [[\tilde{\Phi}_B]] - \frac{\partial \tilde{\Phi}_S}{\partial x_k} n_k \right\} \delta u dS, \quad (\text{A6})$$

where the first two terms represent the variations  $\delta \tilde{\Phi}_B$  and  $\delta \tilde{\Phi}_S$  due to a change in bulk quantities during the virtual displacement of domain wall  $\delta u$ . The last term represents the contribution to the variation  $\delta G$  due to the volume change of domains produced by the virtual displacement of domain wall  $\delta u$  and due to the change of the position of the domain wall. At equilibrium, the variation  $\delta G$  equals the work  $\delta W_p$  produced by external mechanical pressure  $p$  during the virtual displacement of the domain wall

$$\delta W_p = - \int_{S_W} p \delta u dS. \quad (\text{A7})$$

Employing the principle of virtual displacements  $\delta G = \delta W_p$ , it can be readily shown that the first two terms in Eq. (A6) vanish because of the equations of state in the bulk ferroelectric

$$\frac{\partial \Phi}{\partial P_i} = E_i, \quad (\text{A8})$$

Gauss' law for electric displacement  $\partial D_i / \partial x_i = 0$ , and the continuity of the normal component of electric displacement at the domain wall  $[[D_i]] n_i = \sigma_f$ . Finally, the last term in Eq. (A6) yield the formula for the external mechanical pressure on the domain wall

$$p = \left[ \left[ \Phi(P) - \frac{1}{2} \varepsilon_0 E_i E_i - E_i P_i \right] \right] - \widehat{E}_i \sigma_f n_i. \quad (\text{A9})$$

Taking into account the continuity of tangential components of the electric field at the domain wall,  $[[E_{t,i}]] = [[E_i - (E_k n_k) n_i]] = 0$ , continuity of the electrostatic potential at the domain wall  $[[\varphi]] = 0$ , and the algebraic identity (11), we thus arrive at the result announced above, Eq. (13), i.e.:

$$p = [[\Phi(P)]] - \widehat{E}_i ([[P_i]] - \sigma_f n_i). \quad (\text{A10})$$